Translation from German of Patent Application EP 1 142 863 A2

[Patent office data]

(54) Polymerizable Liquid Crystals

(57) The invention relates to polymerizable liquid crystalline compounds characterized by the general formula (I)

[diagram] (I)

wherein A^1 and A^2 are the same or different and each stand for a crosslinkable group; the remainders X are the same or different and each stand for a single bond, -O-, -S-, -C=N-, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -NR-, -O-CO-NR, -NR-CO-O-, $-CH_2-O-$ or -NR-CO-NR, wherein R stands for H or C_1-C_4-alkyl; and M stands for a mesogene group, to a method for their manufacture as well as their application for the manufacture of cholesteric phases.

Description

[0001] The invention relates to a new type of polymerizable liquid crystalline compounds, methods for their manufacture, compositions containing these compounds as well as coating compounds and pigments on the basis of these compounds for diverse application purposes.

[0002] Oriented, low molecular liquid crystals can be fixed permanently by UV-polymerization because UV-polymerization occurs so fast that no relaxation of the oriented liquid crystals is possible. If crosslinkable, cholesteric liquid crystals or crosslinkable mixtures of nematic liquid crystals and chiral doping materials are used, the result, via UV-polymerization, is cholesteric networks which display the optical characteristics of a cholesteric mesophase. It is of special importance that, via the formation of such networks, it can be achieved to stabilize the color flop effect, namely the characteristic of a cholesteric liquid crystal to appear in a different color depending on the viewing angle. Thus, the manufacture of cholesteric effect pigments or color flop pigments can be simplified considerably.

[0003] Cholesteric pigments are form-anisotropic, scale-like particles which are manufactured from photo-crosslinkable, cholesteric starter mixtures. This starter mixture, in its mesophase, must be transformed into an oriented film and fixed by subsequent UV-polymerization. At the same time, the thickness of the scale-like particles is also determined in this step. The resultant cholesteric network then has to be ground to pigment particles in a further process step.

[0004] Cholesteric color flop pigments of various compositions are already known. Color flop pigments on siloxane basis are described, for example, in EP-A-0 601 483. To that end, cyclic siloxanes, which carry chiral as well as mesogene lateral groups, were crosslinked via acrylate or methacrylate groups occurring on the mesogene lateral groups, and processed to pigments.

[0005] Color flop pigments are known from WO-A-97/27252, which are accessible by polymerization of mixtures made of a chiral, liquid crystalline, polymerizable monomer, an achiral liquid crystalline, polymerizable monomer and a chiral compound, and a polymeric bonding agent and/or a monomeric, polymerizable compound and/or an auxiliary dispersion agent. An improved method for the manufacture of color flop pigments as well as numerous different types of crosslinkable cholesteric mixtures are described in WO-A-99/11733. Suitable, achiral liquid crystalline, polymerizable monomers have the general formula

$$Z\text{-}Y\text{-}A\text{-}Y\text{-}M\text{-}Y\text{-}A\text{-}Y\text{-}Z$$

wherein M stands for a mesogene group, A for a spacer group, Y for various bridge groups and Z for a polymerizable end group. Here, preferred remainders Z are acrylate remainders. Preferably, each monomer has two polymerizable groups Z.

[0006] Photo-crosslinkable liquid crystals are known from EP-A-0 675 186, which contain four crosslinkable groups per molecule. These compounds have the following general formula

R-Mesogene-R
|
B
|
R-Mesogene-R

wherein the mesogene represents a triple-core group of linear structure, B a bridge joining the two mesogenes and each R a crosslinkable remainder. The mesogene preferably comprises three bridged p-phenyl groups and the crosslinkable remainders R are each arranged in p-positions at the end. These compounds are used for the manufacture of optical components. Their suitability for the manufacture of crosslinkable cholesteric effect pigments was not investigated. The disadvantage of these compounds is that the achievable network density per mesogene unit is low.

[0007] It is therefore the object of the present invention to provide improved, crosslinkable, achiral, liquid crystalline monomers, in particular those allowing the manufacture of liquid crystalline polymers of higher network density. Surprisingly, this object was solved by the provision of liquid crystalline compounds of formula (I)

[diagram] (I)

wherein

A^1 and A^2 are the same or different and each stand for crosslinkable groups;

the remainders X are the same or different, preferably the same, and each stand for a single bond -O-, -S-, -C=N-, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -NR-, -O-CO-NR, -NR-CO-O-, $-CH_2-O-$ or -NR-CO-NR, wherein R stands for H or C_1-C_4-alkyl; and

M stands for a mesogene group.

[0008] The compounds of formula (I) as per the invention are characterized in that they, on the one hand, are capable of forming a liquid crystalline phase and that, on the other hand, they can stabilize that phase particularly well and durably due to the increased portion of crosslinkable groups.
[0009] A preferred subject of the invention relates to compounds of the general formula (I) whereby A^2 is always in ortho position to A^1.
[0010] Also preferred are compounds of the general formula (I) whereby A^1 and A^2 independently of each other stand for a group of the formula

$$Z\text{-}X\text{-}(Sp)_n\text{-}$$

whereby

Z stands for a crosslinkable remainder;

X has one of the above-mentioned meanings;

Sp stands for a spacer, comprising 1 to 30 C-atoms, whereby the carbon chain is possibly interrupted by oxygen in ether function, sulfur in thioether function or by non-neighboring imino or C_1-C_4-alkyl imino groups; and

n stands for 0 or 1.

Preferably, A^1 and A^2 have the same meaning.

[0011] According to a preferred embodiment, Z is selected amongst:

[diagram]

[diagram]

[diagram]

-N=C=Of-, -N=C=S- and –O-C=N

whereby the remainders R independently stand for C_1-C_4-alkyl such as methyl, ethyl, n or i propyl, or n, i or t butyl.
[0012] According to a preferred embodiment, Sp is selected amongst:

[formula]

[formula]

[formula]

whereby m stands for 1 to 3 and p for 1 to 12.

[0013] According to a further preferred embodiment, M is selected amongst the groups of the general formula (II):

[diagram] (II)

wherein

X has one of the above-mentioned meanings, and

Q may stand for substituted alkylene such as linear or branched C_1-C_{12}-alkylene or may stand for a substituted aromatic bridge group.

[0014] Preferred aromatic bridge groups are selected amongst

[diagram]

and their substituted analogues. Substituted analogues of these bridge groups can carry, per aromatic ring, 1 to 4 of the same or different substituents, preferably one or two substituents per ring or per bridge group. Suitable substituents are selected amongst C_1-C_4-alkyl as per the above definition, nitro, halogen such as F, Cl, Br, I, phenyl or C_1-C_4-alkoxy, whereby the alkyl remainder is defined as above.
[0015] The invention also relates to a method for the manufacture of compounds of the general formula I where a compound of formula III is converted

[diagram] (III)

wherein A^1 and A^2 have the above-mentioned meanings and X' stands for a reactive lateral group, with a mesogene compound of the general formula IV

[formula] (IV)

wherein M has the above-mentioned meanings and X" stands for a reactive lateral group, whereby X' and X" are selected such that they together are capable of forming the X group.
[0016] The invention particularly relates to a method by which a mesogene of formula IV, where X" stands for OH, is converted with a compound of formula III, where X' stands for -COOH or –COHal with Hal = F, Cl, Br, or I.
[0017] The invention furthermore relates to a composition comprising at least one compound of formula I and possibly further constituents selected from cholesteric, possibly crosslinkable compounds, inorganic pigments, dyestuffs, photo-initiators, catalysts, UV-stabilizers, binding agents and possibly polymerizable thinning agents or carriers.
[0018] Preferably used cholesteric compounds are, for example, chiral compounds of the general formulae Xa, b, c and d

[formula] (Xa)

[formula] (Xb)

[formula] (Xc)

[formula] (Xd)

wherein

Z has one of the above-mentioned meanings,

Sp stands for a spacer as per the above definition,

X^2, X^3 and X^4 independently of each other stand for a single chemical bond -O-, -S-, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -O-CO-NR, -NR-CO-O-, or -NR-CO-NR, wherein at least one of the groups X^3 and X^4 mean -O-CO-O-, -O-CO-NR, -NR-CO-O-, or -NR-CO-NR, and R stands for C_1-C_4-alkyl;

X^5 has the meanings given for X^2, X^3 and X^4 or stands for -CH_2-O-, - Of-CH_2-, -CH=N-, -N=CH- or –N=N-,

M stands for a mesogene group as per the above definition,

p^1 stands for a remainder, selected amongst hydrogen, C_1-C_{30}-alkyl, C_1-C_{30}-acyl, C_3-C_8-cycloalkyl, possibly substituted by one to three C_1-C_6-alkyl, and whereby the carbon chain of the alkyl, acyl and cycloalkyl remainders may be interrupted by oxygen in ether function, sulfur in thioether function or by non-neighboring imino or C_1-C_4-alkyl imino groups,

n stands for a number from 1 to 6 and

Ch is a chiral remainder of the value n.

[0019] Ch remainders are, for example,

[18 lines of diagrams]

wherein

L is C_1 to C_4-alkyl, C_1-C_4-alkoxy, halogen, COOR, OCOR, CONHR or NHCOR, and R means C_1-C_4-alkyl.

[0020] (The strokes placed at the end of the listed formulae indicate the free valences).
[0021] Especially preferred are, for example,

[diagrams]

[diagrams]

[diagram] or [diagram]

[0022] These and other preferred chiral components are, for example, mentioned in DE-A 43 42 280 and in the older German patent applications 19520660.6 and 19550704.1.
[0023] A further preferred group used comprises the chiral compounds of formula Xb or Xd wherein

n equals 2,
Z^1 stands for $H_2C{=}CH$- and
Ch stands for a chiral remainder of formula

[diagram] or [diagram]

and
Sp, X^2, X^3, X^4, X^5 and M are defined as above.

[0024] Especially preferred chiral components are the following compounds (A) to (G):

[diagram] (A)

[diagram] (B)

[diagram] (C)

[diagram] (D)

[diagram] (E)

[diagram] (F)

[diagram] (G)

[0025] If the non-chiral compounds of formula I are used in combination with the above chiral compounds, the molar ratio of non-chiral compound of formula I to chiral compound of formulae Xa, b, c, or d is in the range of about 1:0.01 to 1:0.3, in particular 1:0.01 to 1:0.25.
[0026] If one polymerizes the compounds or liquid crystal compositions as per the invention, the state of liquid crystalline arrangement can be fixed. Depending on the polymerizable group, polymerization can take place thermally or photo-chemically, for example. Together with the compounds or liquid crystal compositions as per the invention, other monomers can also be co-polymerized. These monomers can be other polymerizable, liquid crystalline compounds, chiral compounds, which also are preferably polymerized as covalent substances, or common crosslinking agents such as multivalent acrylates, vinyl compounds or epoxides. Especially in the case of isocyanates,

isothiocyanates or epoxides as polymerizable, liquid crystalline compounds, the crosslinking agent preferably is a multivalent alcohol so that urethanes, for example, can be formed. In its quantity, the crosslinking agent must be adapted to the polymerization conditions such that, on the one hand, a satisfactory mechanical stability is achieved and, on the other hand, that the liquid crystalline phase behavior is not affected. Therefore, the amount of crosslinking agent depends on the special application of the polymerizates. For the manufacture of pigments, a greater amount of crosslinking agent is advantageous while for the manufacture of thermoplastic films or for display orientation films, for example, a lower amount of crosslinking agent is required. The amount of crosslinking agent required can be determined by just a few preliminary tests.

[0027] A further modification of the polymerization products made from the compounds or liquid crystal compositions as per the invention is possible by the addition of polymeric auxiliary material prior to polymerization. Such auxiliary materials either should preferably be soluble in the starter mixtures or else in an organic solvent compatible with the starter mixtures. Typical examples of such polymeric auxiliary materials e.g. polyester, cellulose ester, polyurethane as well as polyether or polyester-modified or also unmodified silicones. The required amount of polymeric auxiliary material that may have to be added for the desired result, its chemical nature as well as possibly also quantity and type of solvent are usually well-known by those skilled in the art, or they can also be determined experimentally by a few preliminary tests.

[0028] Apart from compounds of formulae I and Xa to d, further compounds can be mixed in which are built into the polymeric network in a non-covalent manner. These can, for example, be commercially available, nematic liquid crystals.

[0029] Further admixture substances can also be pigments, dyestuffs, filler materials, stabilizers such as UV stabilizers in particular, catalysts, photo-initiators, dispersion agents and similar ones.

[0030] For pigments, these can be inorganic compounds such as iron oxides, titanium oxides and soot, and for the organic compounds e.g. pigments or dyestuffs of the classes monoazo pigments, monoazo dyestuffs as well as their salts, diazo pigments, condensed diazo pigments, isoindoline derivates, derivates of naphthaline or perylene tetra-carbon acid, anthrachinon pigments, thioindigo derivates, azomethine derivates, chinacridone[?], dioxazine, pyrazolochine azolone[?], phthalocyanine pigments or basic dyestuffs such as triaryl methane dyestuffs and their salts.

[0031] A further subject of the invention relates to pigments which comprise at least one compound of formula I in crosslinked form. The compounds as per the invention, of formula I can be processed in combination with conventional chiral compounds, in particular compounds as per the above formulae Xa to d, to cholesteric effect pigments in a manner known in principle. To that end, in a manner known in principle, a crosslinkable mixture of these compounds is applied to a carrier, e.g. by extruding, rolling, dip-wiping, pressing, printing or pouring, the cholesteric phase is formed, i.e. oriented, crosslinked and dried if required. The cholesteric effect layer can then, in a manner known in principle, be removed from the carrier while the flakes obtained are then, if necessary, further shredded and classified. Preferably, pourable mixtures are processed in pouring devices and under conditions as they are described in WO-A-99/11733, and formal reference is herewith made to that paper.

[0032] The layer thickness of the scale-like pigments in this context is 0.5 to 20 μm, in particular 0.5 to 10 μm, as e.g. 0.5 to 3 μm

[0033] The diameter of the pigments as per the invention is about 1 to 500 μm, in particular 3 to 100 μm or 3 to300 μm, and about 2 to 20 times the pigment thickness.

[0034] The pigments can also be formed as multilayer pigments with one or more cholesteric-layers, one or more absorber layers, or one or more pigmented absorber layers. These are, for example, accessible by the processes described in WO-A-99/11719, WO-A-99/11733 or PCT/EP 99/03106, and formal reference is herewith made to those papers.

[0035] A further subject of the invention relates to a coating compound comprising a composition or a pigment as per the above definition. Preferred coating compounds are paints and lacquers in particular, which contain, apart from the pigments and compositions as per the invention, the additives commonly used in paints and lacquers, in particular polymeric binding agents, dispersion agents und thinning agents. Suitable additives are known to those skilled in the art and are described in WO-A-99/11733, and formal reference is herewith made to that paper.

[0036] The invention relates to the use of a compound as per the invention for the manufacture of optical elements such as filters and polarizers, coating compounds, effect foils, cosmetic agents and single or multilayered, cholesteric effect pigments.

[0037] In terms of the invention, all objects are regarded as optical elements, which utilize the optical properties of nematic and/or cholesteric liquid crystals. Individually, as a selection, these can be delay foils, notch filters, color filters for displays, polarizers, but also simply mirrors for decorative purposes. The three-dimensional form of optical elements can be flat, but also curved in a concave or convex shape. As a special embodiment, the polymerized films can also be shredded to pigments and, after mixing with the usual binding agents, can be applied onto carriers by usual application processes such

as extruding, pressing, pouring, spraying, dip-wiping or printing. The preferred embodiment of optical elements is in a flat shape.

[0038] Essential for the quality of the optical elements is the application of the compounds based on general formula I, or mixtures which contain compounds of general formula I, since the optical quality of the coatings is determined by the application method. Generally, suitable application methods are extruding, pressing, rolling, pouring, dip-wiping or printing.

[0039] Here, a preferred embodiment is the dissolving of the liquid crystalline material in a volatile solvent in combination with the possibly necessary additives. Solvents to be used here are THF, MEK, toluol, ethyl acetate and butyl acetate. As additives, polymerization inhibitors or initiators, catalysts, degassing agents, adhesive agents etc. can be used. The isotropic solution is transferred to a substrate via a usual application machine. After passing through a drying tunnel, where the solvent is removed, the wet film can be fixed with the aid of UV radiation. The films obtained thus display a very high reflectivity. These films are eminently suitable as polarizers in LC displays. In one embodiment, several layers of such films are applied on top of each other via lamination coating processes and, by suitable selection of selective wave lengths of the selected films, a polarizer can be obtained covering all light in the visible spectrum (EP 0 720 041).

[0040] Color filters can also be produced with mixtures containing compounds of the general formula I. To that end, the required wave lengths can be applied via common application processes known to those skilled in the art. An alternative type of application utilizes the thermochromism of cholesteric liquid crystals. By setting certain temperatures, the color of the cholesteric layer can be shifted from red via gray to blue. With the aid of masks, certain zones can be polymerized in a targeted manner at defined temperatures. The decisive determining quantity for thermochromism and orientation of the cholesteric mixture, which contains compounds of formula I, is the selection of the chiral auxiliary material. It determines the orientation of the reflected light as well as the thermochromism of the cholesteric system.

[0041] Apart from the optical properties of cholesteric phases, which contain compounds of formula I, the nematic phase of these substances is also suitable for the application in optical elements. Here, the double diffraction of such a system is exploited. In this context, delay foils are to be mentioned most of all.

[0042] In the following, the invention will be explained in detail with the aid of a detailed description of the synthesis of preferred mesogene diols and subsequent synthesis of preferred liquid crystalline, polymerizable monomers of formula I, as per the invention.

A. Synthesis of Mesogene Diols

1. Synthesis of Two-Core Mesogene Diols

[0043] The synthesis of 2,2'-dimethyl-4,4'-dihydroxybiphenyl (1a) takes place by using known methods ([*references*] as per the following reaction diagram 1:

Reaction Diagram 1

[diagram]

[diagram] **1**

[0044] After the acetylation of 4-chlorine-3-methylphenol, the acetylated product is converted to 2,2'-dimethyl-4,4'-diacetyloxybiphenyl by a Ni(0) coupling reaction. The acetyl group is removed by a basic hydrolysis and 2,2'-dimethyl-4,4'-diacetyloxybiphenyl is liberated from the phenolate by the addition of hydrochloric acid. The purification takes place by vacuum distillation and subsequent re-crystallization out of toluol. After purification, mesogene diol can be obtained at a yield of 61%.

2. Synthesis of Triple-Core Mesogene Diols

[0045] The triple-core mesogene diols are composed of a centrally placed hydrochinone unit as well as two 4-hydroxybenzoic acid units placed at the end. They have the following structure:

[diagram]

[0046] The hydrochinone unit, as well as two 4-hydroxybenzoic acid units, may carry one or several substituents R^1-R^4 and X^1-X^4.

[0047] In principle, two approaches can be taken for the synthesis of triple-core mesogene diols. Here, the selection of the synthesis path depends in particular on the substitution pattern of the centrally placed hydrochinone unit, a pattern which determines the synthesis path for the preparation of the triple-core mesogene diol.

[0048] As described in DE-A197 16 822, mesogene diols containing unsubstituted or only methyl-substituted hydrochinone units can be produced as per the following reaction diagram 2, demonstrated by the example of the synthesis of 1,4-phenylene-bis-(4-hydroxy)benzoate (2a):

Reaction Diagram 2

[diagram]

[diagram] **2**

4-hydroxybenzoic acid together with hydrochinone is added to p-xylol in a molar ratio of 2:1. Neither 4-hydroxybenzoic acid nor hydrochinone are fully soluble in p-xylol. By the use of p-toluol sulfone acid (p-TSS) as a catalyst, the triple-core mesogene diol 1,4-phenylene-bis-(4-hydroxy)benzoate, also non-soluble in p-xylol, is obtained as a result of an azeotropic esterification. The mesogene diols produced by this method can be obtained at yields of up to 85%.

[0049] Based on the reaction diagram shown above, the following three triple-core mesogene diols are produced:

Table: Triple-core mesogene diols produced by azeotropic esterification

[diagram]	
[diagram]	**2a**
[diagram]	**2b**
[diagram]	**2c**

[0050] Triple-core mesogene diols, in which the hydrochinone unit carries one or more stericly demanding groups, are preferably produced by a different method. Amongst these stericly demanding groups are tertiary butyl or aryl remainders, for example. The synthesis of such triple-core mesogene diols takes place in accordance with reaction diagram 3 where tertiary butyl hydrochinone is used ([*reference*]).

Reaction Diagram 3

[diagrams]

2d

[0051] 4-hydroxybenzoic acid is protected at the phenolic hydroxy group with chloroformic acid benzylester. This protected 4-hydroxybenzoic acid is subsequently converted with thionyl chloride to the relevant acid chloride. Finally, from the reaction of the acid chloride with tertiary butyl hydrochinone in the presence of triethylamine as an acid-trapping base, hydroxy-protected diester is obtained. The protective groups are removed in a subsequent reaction step by catalytic hydration at a palladium catalyst. The mesogene diols produced on the basis of these instructions can be obtained at yields of up to 40%. The low overall yield is the result of low yields in the production of benzyl-protected mesogene diols. Based on this reaction diagram, for example, the triple-core mesogene diols listed in the following table can be produced.

Table: Triple-core mesogene diols that carry stericly demanding groups

[diagram]	
[diagram]	**2d**
[diagram]	**2e**

[diagram]	**2f**

3. Synthesis of Four-Core Mesogene Diols

[0052] The reactions described above for the synthesis of triple-core mesogene diols can also be applied to four-core mesogene diols. Structurally, the four-core mesogene diols are differentiated from the triple-core ones in that just the middle part of the molecule does not consist of one hydrochinone unit but of a two-core, aromatic diol component. In the following table, examples of two useful four-core mesogene diols as per the invention are summarized. The manufacture took place by azeotropic esterification in p-xylol with p-toluol sulfone acid as a catalyst. The yields reached values of up to 77%.

Table: Four-core mesogene diols that were produced by azeotropic estrification

[diagram]	
[diagram]	**3a**
[diagram]	**3b**

B. Synthesis of New Liquid Crystalline Tetra-Acrylates

[0053] Preferred liquid crystalline tetra-acrylates are accessible via 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid. 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid is synthesized in a known manner ([reference]). The synthesis is illustrated in the following reaction diagram:

Reaction Diagram 4

[diagrams]

12

[0054] In a first step, basic etherification of ethyl-3,4-dihydroxy-benzoate takes place in the presence of 6-chlorohexanol. Subsequently, the ethylester was saponified with methanolic potash lye so that the free acid could be isolated. This was then esterified with acrylic acid chloride in 1,4-dioxane whereby di-ethylaniline was used as a base for trapping the liberated hydrochloric acid. In a second step, the acid is then transformed into the acidic chloride and converted with various mesogene diols. This second step is illustrated in the following reaction diagram 5:

Reaction Diagram 5

[diagrams]

12 **13**

[diagram] **14**

[diagram]	
[diagram]	**2a**
[diagram]	**2b**
[diagram]	**3a**
[diagram]	**3b**

[0055] To that end, 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid was converted to acidic chloride with oxalyl chloride. Subsequently and without further purification, this was brought to a reaction at a ratio

of 2:1, with the relevant mesogene diol in THF. Here, tri-ethylamine served as a base in order to bind the hydrochloric acid resulting from the esterification. The tetra-acrylates produced in that manner were subsequently purified in column-type chromatography. The yield of tetra-acrylates was between 42% and 72%.

[0056] The structures of the tetra-acrylates synthesized in accordance with the above reaction diagram are summarized in the following table.

Table: Synthesized tetra-acrylates and their mesophase behavior

[diagram]	**14a**
[diagram]	**14b**
[diagram]	**14c**
[diagram]	**14d**

a) DSC, 2. heating period, inhibitor content: 2% sulfur by weight, heating rate 10 K/min
b) Polarizing microscope
c) Cr = crystalline; N = nematic; I = isotropic

[0057] The phase behavior of the tetra-acrylates was examined with the aid of DCS and polarizing microscopy. 2% sulfur by weight was added as inhibitor in order to prevent thermal polymerization during this examination. A nematic mesophase could be detected with all four tetra-acrylates. Of the tetra-acrylates with a five-core mesogene unit, **14a** shows a nematic mesophase between 121°C and 127°C and **14b** a nematic mesophase between 107°C and 122°C. The methyl substitution at the mesogene unit lowers both the melting point as well as the purification point when compared with the unsubstituted system **14a**. It is noteworthy that the influence of the substituent on the melting point is considerably more pronounced than the influence on the purification point.

[0058] Of the tetra-acrylates with a six-core mesogene unit, **14c** shows a nematic mesophase between 123°C and 155°C. The tetra-acrylate **14d** also behaves nematically. However, for this tetra-acrylate, the nematic mesophase in the heating curve of the DSC cannot be detected, while a fluid mesophase between 132°C and 143°C can be detected under the polarizing microscope. The DSC shows a mesophase in the cooling curve only, with a clearly discernible transition between isotropic and nematic phase. Due to the introduction of the two methyl groups, the phase width in comparison to **14c** becomes considerably smaller. It is interesting that the melting point increases with the introduction of two methyl groups while the introduction of one methyl group led to a lowering of the melting point for **14b**. The DCS measurements on **14b** and **14c** show additional transitions in the crystalline range. These transitions were not examined any further.

[0059] Starting with the specific instructions above, those skilled in the art can undertake common variations of the specifically described processes in order to develop further compounds as per the invention.

[0060] At this point, the invention will be explained in more detail by referring to the following embodiments.

Experimental Part

[0061] Instruments and auxiliary devices

IR Spectroscopy	[Make & Model]
^{1}H-NMR Spectroscopy	[Make & Model]
^{13}C-NMR Spectroscopy	[Make & Model]
DCS	NIKON Diaphot with Mettler heating table
Polarizing Microscopy	FP82, Mettler FP90 control unit

Chemicals and solvents

[0062] Dioxane was dried by heating while recirculating across potassium and distilled off under gas shielding. Tetrahydrofurane was initially heated while recirculating across potassium hydroxide, distilled off, heated again while recirculating across potassium and finally distilled off under gas

shielding. Methylene chloride was dried by heating while recirculating across potassium hydride and distilled off under gas shielding. All further solvents were distilled via filler body columns and used without further drying. Triethylamine was heated while recirculating across potassium hydroxide and distilled off under gas shielding. Acrylic acid chloride was purified by double fractionated distillation under gas shielding with 2,6-di-tertiary-butyl-p-cresol as a stabilizer. All other chemicals used were commercially available in sufficiently high purity and thus were used without any further purification.

Reference example 1: Manufacture of mesogene diols

[0063] The following mesogene diols were produced:

Mesogene diols:

1	[diagram]
	[diagram]
2a	[formula]
2b	[formula]
2c	[formula]
2d	[formula]
2e	[formula]
2f	[formula]
	[diagram]
3a	[formula]
3b	[formula]

Reference example 1.1: Manufacture of 2,2'-dimethyl-4,4'-dihydroxy-biphenyl (1)

a) 4-chloro-3-methyl-phenylacetate

[0064] In a 250 mL bulb with recirculating cooler, 43.0 g (0.30 mol) of 4-chloro-3-methylphenol, 34 mL (0.36 mol) of acetic acid hydride and a few drops of concentrated sulfuric acid are stirred for 2 h at 60°C. After cooling down to room temperature, the reaction mixture is poured into 200 mL of water and stirred for 1 h at room temperature. Subsequently, one extracts with 400 mL diethylether [*German sentence appears to be incomplete*]. The organic phase is dried on magnesium sulfate and the ether is distilled off. The raw product is subsequently distilled in a vacuum (melting point 65-68°C, 20 mbar).
Yield: 52.5 g (95% of the theoretical yield) as a colorless liquid.
Characterization:
[sequence of numbers and abbreviations]

b) 2,2'-dimethyl-4,4'-dihydroxy-biphenyl

[0065] 2.08 g (0.016 mol) of nickel dichloride, 20.9 g (0.080 mol) of triphenyl-phosphane (PPh_3), 30.1 g (0.460 mol) of zinc powder, 2.51 g (0.016 mol) of 2,2'-bipyridine (bpy) and 160 mL of dimethylacetamide (DMAc) are placed in a 500 mL bulb with recirculating cooler. This reaction mixture is heated to 65°C. After the addition of 52.5 g (0.285 mol) of 4-chloro-3-methyl-phenylacetate, the reaction mixture is stirred for 4 h at 70°C. After cooling down to room temperature, the reaction mixture is filtered, subsequently poured onto a 2.5-molar sodium hydroxide solution and stirred overnight. After washing with 300 mL diethylether, the watery phase is acidified with concentrated hydrochloric acid (pH = 1). Subsequently, the watery phase is extracted with 800 mL of diethylether and the diethylether is distilled off. The raw product is distilled in a vacuum (melting point 167-170°C, 0.01 mbar) and subsequently recrystallized twice out of toluol.
Yield: 18.5 g (61% of the theoretical yield) as a white solid.
Characterization:
[sequence of numbers and abbreviations]
Melting point: 137-138°C

Reference example 1.2: Preparation of mesogene diols with the aid of azeotropic esterification

[0066]

A) General operating instructions: The relevant 4-hydroxybenzoic acid and the relevant aromatic diol together with p-toluol-sulfonic acid in p-xylol are placed in a bulb with a water trap and heated for 24 h while recirculating. After water separation has been completed, the reaction mixture is left to cool down to room temperature and the raw product is filtered out.

B) Compounds produced in accordance with the general operating instructions:

a) 1,4-phenylene-bis-(4-hydroxybezoate (2a)

[0067] Purification: The raw product is made into a suspension in 100 mL of ethanol, stirred for several hours at room temperature and subsequently filtered out. The product is obtained as a white solid.

Formulation	3.30 g	(0.03 mol)	Hydrochinone
	8.29 g	(0.06 mol)	4-Hydroxybenzoic acid
	0.60 g	(0.003 mol)	p-Toluol-sulfonic acid
	150 mL		p-Xylol

Yield: 8.50 g (81% of the theoretical yield) as a white solid.
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 294°C

b) 2-methyl-1,4-phenylene-bis-(4-hydroxy)benzoate (2b)

[0068] Purification: The raw product is made into a suspension in 100 mL of diethylether, stirred for several hours at room temperature and subsequently filtered out. The product is obtained as a white solid.

Formulation	3.72 g	(0.03 mol)	2-Methyl-hydrochinone
	8.29 g	(0.06 mol)	4-Hydroxybenzoic acid
	0.60 g	(0.003 mol)	p-Toluol-sulfonic acid
	150 mL		p-Xylol

Yield: 9.31 g (85% of the theoretical yield) as a white solid.
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 276°C

c) 2,3,5-trimethyl-1,4-phenylene-bis-(4-hydroxy)benzoate (2c)

[0069] Purification: The raw product is made into a suspension in 100 mL of diethylether, stirred for several hours at room temperature and subsequently filtered out. Then, the raw product is recrystallized out of 1000 mL of methanol. The product is obtained as a white solid.

Formulation	4.56 g	(0.03 mol)	2,3,5-Trimethyl-hydrochinone
	8.29 g	(0.06 mol)	4-Hydroxybenzoic acid
	0.60 g	(0.003 mol)	p-Toluol-sulfonic acid
	150 mL		p-Xylol

Yield: 6.65 g (57% of the theoretical yield) as a white solid.
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 298°C

d) 4,4'-biphenylene-bis-(4-hydroxy)benzoate (3a)

[0070] Purification: Recrystallization out of 1500 mL of cyclohexanon.

Formulation	8.75 g	(0.047 mol)	4,4'-Dihydroxy-biphenyl

	12.98 g	(0.094 mol)	4-Hydroxybenzoic acid
	2.00 g	(0.01 mol)	p-Toluol-sulfonic acid
	250 mL		p-Xylol

Yield: 15.40 g (77% of the theoretical yield)
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 320°C

e) 2,2'-dimethyl-4,4'-biphenylene-bis-(4-hydroxy)benzoate (3b)

[0071] Purification: Recrystallization out of 700 mL of 1,4-dioxane.

Formulation	9.43 g	(0.044 mol)	4,4'-2,2'-Dimethyl-dihydroxy-biphenyl
	12.19 g	(0.088 mol)	4-Hydroxybenzoic acid
	2.00 g	(0.01 mol)	p-Toluol-sulfonic acid
	250 mL		p-Xylol

Yield: 14.73 g (74% of the theoretical yield)
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 242°C

e) 2,2'-dimethyl-4,4'-biphenylene-bis-(4-hydroxy)benzoate (3b)

<u>Reference example 1.3:</u> Preparation of mesogene diols via protected 4-hydroxybenzoic acids

A) General operating instructions

i) Introduction of a protection group at the hydroxy function of 4-hydroxybenzoic acid

[0072] The relevant 4-hydroxybenzoic acid is dissolved in 1 M of watery sodium lye. At 0°C, chiroformic acid benzylester is added in droplets. The reaction mixture is stirred for 2 h and subsequently poured into 2 M of hydrochloric acid. The precipitation obtained is filtered off and recrystallized.

ii) Preparation of hydroxy-protected mesogene diols

[0073] The protected 4-hydroxybenzoic acid is dissolved in 1,2-dichloroethane. Thionylchloride is mixed into the solution which is subsequently heated for 2 h while recirculating. The solvent and 'unreacted' thionylchloride are distilled off under vacuum. The resultant acid chloride is dissolved in 1,2-dichloroethane and added in droplets to a solution of an aromatic diol and triethylamine in 1,2-dichloroethane. This reaction mixture is heated for 2 h while recirculating, and subsequently cooled down to room temperature and filtered. 1,2-Dichloroethane is distilled off under vacuum, the residue is absorbed in chloroform and washed with water. The organic phase is dried on Na_2SO_4. Subsequently, the chloroform is distilled off and the raw product is purified by recrystallization.

iii) Liberation of the mesogene diol by catalytic removal of the protection groups

[0074] The protected mesogene diol together with palladium is placed onto active charcoal (5%) in tetrahydrofurane. This reaction mixture is saturated with hydrogen and subsequently stirred overnight at 40°C in a hydrogen atmosphere. Subsequently, the reaction mixture is filtered and the THF is distilled off.

B) Compounds produced in accordance with the general operating instructions:

a) Benzyloxy-4-hydroxybenzoic acid

[0075] Purification: Recrystallization out of 1200 mL of acetone/water at 1:1

Formulation	20.00 g	(0.143 mol)	4-Hydroxybenzoic acid
	29.6 g	(0.173 mol)	Chloroformic acid benzylester
	300 mL		1 M sodium lye
	500 mL		2 M hydrochloric acid

Yield: 29.3 g (75% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

b) Benzyloxy-4-hydroxyvanillin acid

[0076] Purification: Recrystallization out of a mixture of 450 mL of water and 250 mL acetone.

Formulation	18.90 g	(0.11 mol)	Vanillin acid
	25.60 g	(0.15 mol)	Chloroformic acid benzylester
	400 mL		1 M sodium lye
	1000 mL		2 M hydrochloric acid

Yield: 20.3 g (61% of the theoretical yield)
Characterization:
[sequence of numbers and abbreviations]

c) 2-tertiary butyl-1,4-phenylene-bis-(4-benzylcarbonato)benzoate

[0077] Purification: Recrystallization out of 1000 mL of cyclohexane

Formulation	35.52 g	(0.13 mol)	Benzyloxy-4-hydroxybenzoic acid
	12 mL	(0.17 mol)	Thionchloride
	150 mL		1,2-Dichloroethane
	9.72 g	(0.06 mol)	Tertiary butylhydrochinon
	37 mL	(0.26 mol)	Triethylamine
	200 mL		1,2-Dichloroethane

Yield: 17.2 g (43% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

d) 2-Phenyl-1,4-phenylene-bis-(4-benzylcarbonato)benzoate

[0078] Purification: Recrystallization out of 1000 mL of cyclohexane

Formulation	29.3 g	(0.11 mol)	Benzyloxy-4-hydroxybenzoic acid
	12 mL	(0.17 mol)	Thionchloride
	150 mL		1,2-Dichloroethane
	7.91 g	(0.043 mol)	Phenylhydrochinon
	31 mL	(0.22 mol)	Triethylamine
	200 mL		1,2-Dichloroethane

Yield: 16.0 g (54% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

e) 2-tertiary butyl-1,4-phenylene-bis-(3-methoxy-4-benzylcarbonato)benzoate

[0079] Purification: From a THF solution re-precipitated in ice water

Formulation	12.04 g	(0.04 mol)	Benzyloxy-vanillin acid
	7.3 mL	(0.1 mol)	Thionchloride
	70 mL		1,2-Dichloroethane
	2.66 g	(0.016 mol)	Tertiary butylhydrochinon
	11.4 mL	(0.08 mol)	Triethylamine
	130 mL		1,2-Dichloroethane

Yield: 5.98 g (51% of the theoretical yield)
Characterization:
[sequence of numbers and abbreviations]

f) 2-tertiary butyl-1,4-phenylene-bis-(4-hydroxy)benzoate (2d)

[0080]

Formulation	22.6 g	(0.033 mol)	2-Butyl-1,4-phenylene-bis-(4-benzylcarbonato)benzoate
	2.5 g		Palladium on active charcoal (5%)
	200 mL		THF

Yield: 12.0 g (89% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 288°C

g) 2-Phenyl-1,4-phenylene-bis-(4-hydroxy)benzoate (2e)

[0081]

Formulation	15.9 g	(0.023 mol)	2-Phenyl-1,4-phenylene-bis-(4-benzylcarbonato)benzoate
	2.5 g		Palladium on active charcoal (5%)
	200 mL		THF

Yield: 9.5 g (96% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]
Disintegration (T_{on}): 290°C

h) 2-Tertiary butyl-1,4-phenylene-bis-(3-methoxy-4-hydroxy)benzoate (2f)

[0082] Purification: From isopropanol re-precipitated in water

Formulation	11.45 g	(0.016 mol)	2-Tertiary butyl-1,4-phenylene-bis-(3-methoxy-4-benzylcarbonato)benzoate
	1 g		Palladium on active charcoal (5%)
	100 mL		THF

Yield: 4.7 g (63% of the theoretical yield) as a yellowish solid
Characterization:
[sequence of numbers and abbreviations]
Melting point: 116°C

<u>Reference example 2:</u> Manufacture of crosslinkable spacer units 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid

[0083]

[diagram]

a) 3,4-Di-(6-acryloyloxy-hexyloxy)benzoic acid

[0084] 10.93 g (0.06 mol) of 3,4-dihydroxybenzoic acid ethylester are placed into 200 mL of 2-butanon. After the addition of 5.3 g (0.133 mol) of sodium hydroxide, 19.9 g (0.133 mol) of sodium iodide and 17.74 g (0.133 mol) of 6-chlorohexanol, the reaction mixture is stirred for 20 h at 60°C. Subsequently, the 2-butanon is distilled off. The residue is absorbed by 300 mL 0.4 M of a sodium hydroxide solution and extracted, four times, with 100 mL of diethylether. The ether phases are merged and concentrated at a rotary evaporator. The residue is dissolved in 200 mL of methanol. After the addition of 60 mL of a 4.5 M sodium hydroxide solution, the reaction mixture is stirred for

20 h while recirculating. After concentration of the reaction mixture at a rotary evaporator, the residue is absorbed by 200 mL 0.4 M of a sodium hydroxide solution and washed, three times, with 100 mL of diethylether. The watery phase is subsequently acidified with concentrated hydrochloric acid (pH = 1). The precipitated product is filtered off and recrystallized out of 500 mL of water.
Yield: 14.3 g (67% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]
Melting point: 133-135°C

b) 3,4-Di-(6-acryloyloxy-hexyloxy)benzoic acid

[0085] 13.6 g (0.04 mol) of 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid, 9.6 g (0.06 mol) of N,N-diethyl-aniline and 100 mg of 2,6-di-tertiary-butyl-p-cresol as a stabilizer are placed into 150 mL of-1,4-dioxane and heated to 60°C. At 60°C, 6.9 mL (0.085 mol) of acrylic acid chloride is added as droplets at a slow rate so that the reaction temperature will not exceed 65°C. The reaction mixture is stirred for 2.5 h at 60°C. After the solution has cooled down to room temperature, it is poured onto ice water while being stirred. A precipitation of 3,4-di-(6-acryloyloxy-hexyloxy)benzoic acid is obtained, dried and recrystallized out of isopropanol.
Yield: 13.1 g (71% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]
Melting point: 90-92°C

<u>Example 1</u>: Preparation of tetra-acrylates

[0086] The following tetra-acrylates were manufactured:

Tetra-acrylates:

[diagram]

14a [formula]
14b [formula]

[diagram]

14c [formula]
14d [formula]

A) General operating instructions for the preparation of tetra-acrylates with the aid of acidic chloride

i) Preparation of the acidic chloride

[0087] The relevant spacer-carrying hydroxybenzoic acid is suspended in methylene chloride. While applying cooling with ice, an 8 to 10 molar excess of oxalyl chloride is added slowly in droplets. This reaction mixture is stirred at room temperature until no further gas development can be observed. A clear solution is obtained from which the methylene chloride and 'unreacted' oxalyl chloride is distilled off under vacuum. The residual acidic chloride is converted further without further purification.

ii) Conversion of the acidic chloride with mesogene diols

[0088] The relevant mesogene diol together with triethylamine and 2,6-di-tertiary-butyl-p-cresol as a stabilizer (for acrylates only) is placed in THF. The acid chloride is dissolved in THF and added in droplets while being cooled by ice. Subsequently, this mixture is stirred for 24 h at room temperature. Then, the mixture is filtered and concentrated at the rotation evaporator. The residue is absorbed by chloroform and extracted with water three times. The solvents are then evaporated, the raw product obtained is dried under vacuum and purified by re-crystallization or column chromatography.

B) Tetra-acrylates produced in accordance with the general operating instructions:

a) Tetra-acrylate **14a**

[0089] Purification: Column chromatography (chloroform: acetic acid ethylester 40:1)

Formulation	3.55 g	(7.68×10^{-3} mol)	3,4-Di-[6-(acryloyloxy-hexyloxy)]benzoic acid
	6 mL	(0.070 mol)	Oxalyl chloride
	40 mL		Methylene chloride
	1.21 g	(3.45×10^{-3} mol)	1,4-Phenylene-bis-(4-hydroxy)-benzoate
	2 mL	(0.014 mol)	Triethylamine
	100 mL		THF
	50 mg		2,6-Di-tertiary-butyl-p-cresol

Yield: 1.84 g (43% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

[0090] Thermal behavior: Cr 121 N 127 I (DSC, 2. heating up, heating rate 10 K/min, 2% sulfur by weight).

b) Tetra-acrylate **14b**

[0091] Purification: Column chromatography (chloroform: acetic acid ethylester 40:1)

Formulation	2.00 g	(4.32×10^{-3} mol)	3,4-Di-[6-(acryloyloxy-hexyloxy)]benzoic acid
	3.5 mL	(0.041 mol)	Oxalyl chloride
	30 mL		Methylene chloride
	0.71 g	(1.94×10^{-3} mol)	1,4-Methyl-1,4-phenylenebis-(4-hydroxy)-benzoate
	1 mL	(0.007 mol)	Triethylamine
	80 mL		THF
	50 mg		2,6-Di-tertiary-butyl-p-cresol

Yield: 1.65 g (68% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

[0092] Thermal behavior: Cr 107 N 122 I (DSC, 2. heating up, heating rate 10 K/min, 2% sulfur by weight).

c) Tetra-acrylate **14c**

[0093] Purification: Column chromatography (chloroform: acetic acid ethylester 40:1)

Formulation	3.04 g	(6.57×10^{-3} mol)	3,4-Di-[6-(acryloyloxy-hexyloxy)]benzoic acid
	5 mL	(0.058 mol)	Oxalyl chloride
	40 mL		Methylene chloride
	1.26 g	(2.95×10^{-3} mol)	4,4'-Biphenylene-bis-(4-hydroxy)-benzoate
	1.5 mL	(0.01 mol)	Triethylamine
	100 mL		THF
	50 mg		2,6-Di-tertiary-butyl-p-cresol

Yield: 2.79 g (72% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]

[0094] Thermal behavior: Cr 123 N 155 I (DSC, 2. heating up, heating rate 10 K/min, 2% sulfur by weight).

d) Tetra-acrylate **14d**

[0095] Purification: Column chromatography (chloroform: acetic acid ethylester 40:1)

Formulation	3.05 g	(6.60×10^{-3} mol)	3,4-Di-[6-(acryloyloxy-hexyloxy)]benzoic acid
	5.5 mL	(0.064 mol)	Oxalyl chloride
	40 mL		Methylene chloride
	1.34 g	(2.95×10^{-3} mol)	2,2'-Dimethyl-4,4'-biphenylene-bis-(4-hydroxy)benzoate

	1.5 mL	(0.01 mol)	Triethylamine
	100 mL		THF
	50 mg		2,6-Di-tertiary-butyl-p-cresol

Yield: 1.66 g (42% of the theoretical yield) as a white solid
Characterization:
[sequence of numbers and abbreviations]
[0096] Thermal behavior: Cr 132 N 143 I (polarizing microscope)

Example 2: Manufacture of a cholesteric liquid crystal mixture

[0097] A solution comprising 20 parts of a cholesterin mixture comprising 93.85% by weight of the achiral tetra-acrylate **14c** and 6.15% by weight of the chiral compound of formula B

[diagram] (B)

is dissolved with 3 parts of the photo-initiator Irgacure 184 (1-hydroxy-cyclohexylphenyl ketone) in 77 parts of methylethyl ketone. The mixture obtained thus was, as described in WO-A-99/11733, applied to a 15 μm thick polyethylene-terephthala foil with the aid of a pouring device, dried at 60°C and crosslinked by radiation with UV light. The dry coating thickness was 2.5 μm. The coating displayed a coloring of λ_{max} = 611 nm, dependent on the viewing angle.

Patent Claims

1. Polymerizable liquid crystalline compounds **characterized by** the general formula (I)

[diagram] (I)

whereby

A^1 and A^2 are the same or different and each stand for a crosslinkable group;

the remainders X are the same or different and each stand for a simple compound -O-, -S-, -C=N-, -O-CO-, -CO-O-, -O-CO-O-, -CO-NR-, -NR-CO-, -NR-, -O-CO-NR, -NR-CO-O-, $-CH_2-O-$ or -NR-CO-NR, wherein R stands for H or C_1-C_4-alkyl; and

M stands for a mesogene group.

2. Compounds according to claim 1 **characterized in that** A^2 is always in ortho position to A^1.

3. Compounds according to one of the previous claims **characterized in that** A^1 and A^2 independently of each other stand for a group of the formula

$$Z\text{-}X\text{-}(Sp)_n\text{-}$$

whereby

Z stands for a crosslinkable remainder;

X has one of the above-mentioned meanings;

Sp stands for a spacer, comprising 1 to 30 C-atoms, whereby the carbon chain is possibly interrupted by oxygen in ether function, sulfur in thioether function or by non-neighboring imino or C_1-C_4-alkyl imino groups; and

n stands for 0 or 1.

4. Compounds according to claim 3 **characterized in that** Z is selected from:

[diagram]

[diagram]

[diagram]

-N=C=Of-, -N=C=S- and –O-C=N

whereby the remainders R independently of each other stand for C_1-C_4-alkyl.

5. Compounds according to claims 3 or 4 **characterized in that** Sp is selected from:

[formula]

[formula]

[formula]

[formula]

whereby m stands for 1 to 3 and p for 1 to 12.

6. Compounds according to one of the previous claims **characterized in that** M is selected from groups of the general formula II:

[formula] (II)

whereby

X has above-mentioned meanings, and

Q may stand for substituted alkylene or for a substituted aromatic bridge group.

7. Compounds according to claim 6 **characterized in that** the aromatic bridge group is selected from

[diagram]

and their substituted analogues.

8. A method for the manufacture of compounds according to claim 1 **characterized in that** the compounds of formula III

[diagram] (III)

wherein A^1 and A^2 have the above-mentioned meanings and X' stands for a reactive lateral group, are converted with a mesogene compound of the general formula IV

[formula] (IV)

wherein M has the above-mentioned meanings and X" stands for a reactive lateral group, whereby X' and X" are selected such that they together are capable of forming the X group.

9. A method according to claim 8 whereby a mesogene of formula IV, where X" stands for OH, is converted with a compound of formula III, where X' stands for -COOH or –COHal with Hal = F, Cl, Br, or I.

10. A composition comprising at least one compound according to claims 1 to 7 and possibly further constituents selected from cholesteric, possibly crosslinkable compounds, inorganic pigments, dyestuffs and possibly polymerizable thinning agents or carriers.

11. Pigments comprising at least one compound according to claims 1 to 7 in crosslinked form.

12. Coating compound comprising a composition according to claim 10 or a pigment according to claim 11.

13. Application of a compound according to claims 1 to 7 for the manufacture of optical elements, such as in particular filters and polarizers, coating compounds, effect foils, cosmetic agents and single or multi-layered cholesteric effect pigments.